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VARIABILITY OF LA, SC, TH AND U CONTENTS IN BITUMINOUS COALS OF LUBLIN FORMATION IN LUBLIN COAL BASIN (LCB)

Abstract

As compared with international coals, high contents of La, Sc, Th and U were found in LCB coals. La content in Polish coals was determined for the first time. Vertical and lateral variability in element contents of the Lublin Formation, where they occur in associations with other elements, was noted.

Key words: geochemical characteristics La, Sc, Th, U, coal.

Introduction

Following geological studies and mining conducted during recent 20 years, it was possible to access LCB coal seams and to discover which elements, not yet determined or determined rarely, occur in coals. In this study, we decided to analyse coals from coal seams (378, 382, 385, 387, 389, 391, 394) marked by the largest spread, according to Porzycki and Zdanowski [11] and relatively stable thickness in Bogdanka and Chełm deposits. The seams are supposed to be mined in the coal mine „Lubelski Węgiel Bogdanka” [1].

The aim of this article is to evaluate average contents and changes in La, Sc, Th and U contents in LCB coals.

Scope of research and methodology

From seams 382 and 385/2 coal columns were sampled in active mine faces in the coal mine „Bogdanka”. 219 coal samples from drill cores in 12 holes in the deposit „Chełm” were obtained for research from the Polish Geological Institute, the Upper Silesian Branch, as part of the Marie Skłodowska-Curie Fund. The results were submitted to the Institute and published [2, 7, 8, 9]. 30 coal samples not studied so far due to small coal mass, collected from 8 drill cores (Fig. 1), were analysed in this work. In coal ashes (525oC), La, Sc, Th and U contents were determined with ICP–Mass Spectrometer (Tab. 1).

By means of X2 Pearson's test, geometric means were considered best to estimate averages (Tab. 2), therefore the test was also used to determine average La, Sc, Th and U contents in coal seams of the profile of the Lublin Formation (Fig. 2). Moreover, correlation coefficients were calculated to obtain element affinity to organic or mineral portions of the investigated coals, and to find element associations marked by geochemical relationships (Tab. 3).

Results and interpretation

Coal ash

Average ash content in LCB coals is 11.88%, which is slightly lower than ash content in the whole basin as given by Cebulak ($A = 13.63\%$) [2], and Porzycki and Zdanowski ($A = 14.82\%$) [11]. Since average ash contents in bituminous coals around the world have not been estimated so far, the investigated coals were compared to petrologically similar Paleozoic coals from other seams in the North Atlantic macro-region. Based on the comparison, ash content in the LCB coals was determined to range

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from 1.34% to 24.20% corresponding to ash contents in English [16] and American [14] coals.

Generally, 1-modal distribution of ash contents in the coals of the profile of the LCB, with maximum ash content in coal from the coal seam 387, and minimum – in the coal from the seam 394 (Fig. 2) was discovered. Large differences in ash contents were determined in coals within the LCB and vertical profile of the seams 378 and 391 (Tab. 1). The changes result probably from the differences in mineral matter content within the LCB coal seams described by Knafel [6].

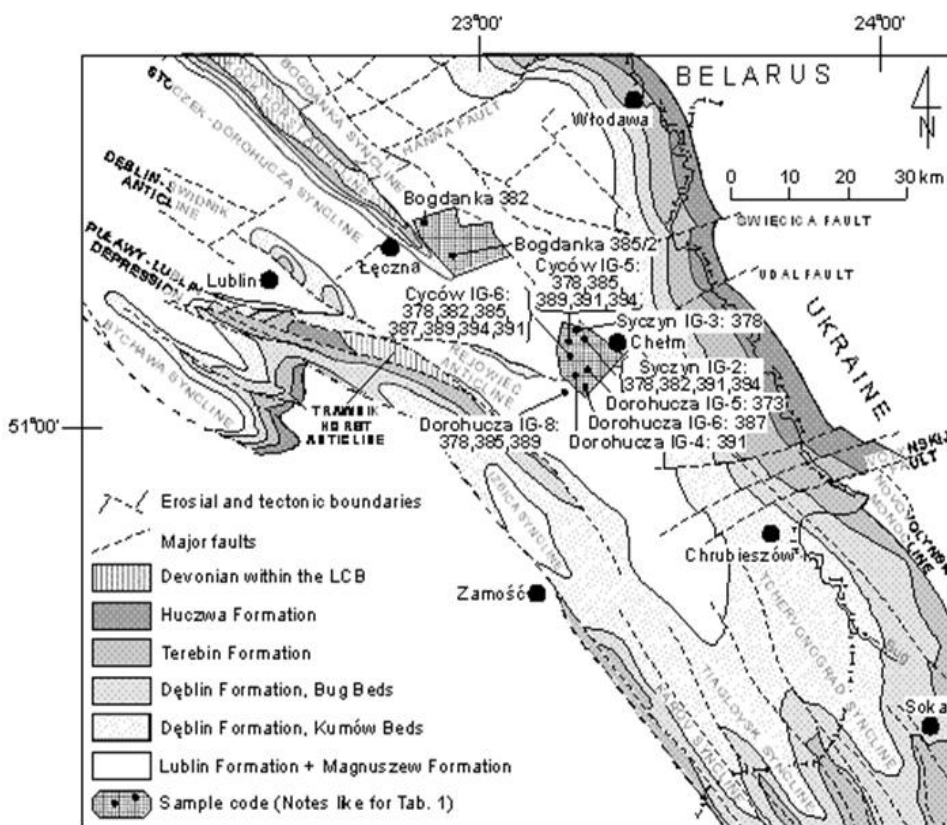


Fig. 1 A geological characteristics of the researched areas in the LCB (after Porzycki and Zdanowski, 1995) and location of the places from where symplex were taken

Table 1 La, Sc, U and Th content (ppm) in coal form researched areas in the LCB

Sample	Seam	Borehole, Mine	Seam ticknes (m)	Ash ₅₂₅ (%)	Content of elements (g/Mg)			
					La	Sc	Th	U
L	378	Cyców IG-6	1,30	10,78	73	63	9	10
38L		Cyców IG-5	0,35	6,60	117	128	29	19
90L		Syczyn IG-3	0,80	16,73	64	68	27	10
105L		Syczyn IG-2		17,17	82,4	62,3	30,5	11,9
106L			3,10	15,85				
107L				31,16				
207L		Dorohucza IG-1	2,40	22,93	50	64	20	10
10L	382	Cyców IG-6	3,60	9,80	112,4	63,7	40,9	15,2
11L				15,07				
111L		Syczyn IG-2	0,40	13,46	57	32	22	10
64W		Bogdanka	2,52	18,62	58	85	31	18
16L	385	Cyców IG-6	0,90	17,70	66	32	38	24
45L		Cyców IG-5	1,20	14,81	213	33	54	10
213L		Dorohucza IG-8	1,10	27,75	121	45	35	23
62W		Bogdanka	1,27	8,48	48	56	28	16
18L	387	Cyców-IG-6	0,30	10,43	207	84	48	43
201L		Dorohucza IG-6	2,40	22,93	98	24	53	10
19L	389	Cyców IG-6	2,80	33,50	57	28	22	10
48L		Cyców IG-5	0,80	5,00	52	85	20	30
215L		Dorohucza IG-8	1,00	16,92	55	54	26	10
21L	391	Cyców IG-6	2,90	8,29	51,5	26,1	23,7	14,3
22L				21,30				
49L		Cyców IG-5	2,60	6,60	56	69	23	10
116L		Syczyn IG-2	2,50	7,41	54	37	22	15
177L		Dorohucza IG-4	1,00	7,69	58	20	13	10
23L	394	Cyców IG-6	3,30	15,84	62,7	32,1	25,5	13,9
25L				16,67				
26L				14,62				
52L		Cyców IG-5	1,10	3,67	42	133	23	25
119L		Syczyn IG-2	0,50	4,73	33	106	16	18

Lanthanum

Average La contents in the LCB coals is found to be much higher than in international coals (Tab. 2). A wide La content interval in the investigated coals and quite a high standard deviation result from statistically significant vertical and lateral variability of La content in the LCB coals. La distribution in the coals of the profile of the Lublin Formation is approximately 1-modal, with maximum content in coal from the seam 387, and minimum content in coal from the seam 394 (Fig. 2). In general, insignificant differences in La contents in coals within the coal seams 387>382>378>394>391=389 were discovered (Tab. 1). However, visible changes in La contents in the coal of the vertical profile in seams 382>378> 394=391 result probably from La sorption from aqueous solutions infilling the seam by organic matter and clay mineral aggregates in the areas near the roof and the floor of the coal seams. The process was discussed in detail by Rysanov and Yudovich [13].

The correlation coefficient between La content in the investigated coals and ash content indicates that both organic and mineral matter have influence on La accumulation in coal (Tab. 3). Strong correlation bond between La and Th, moderately strong bond between La and Nb>V=Zr>Cu>Y, and weak bond between La, and Ba and Cr were discovered. On the other hand, the presence of Mg and Mn in the coals almost completely excludes the possibility for La to occur in the LCB coals.

The results of geochemical studies on the coals from different coal seams of the world by various authors compiled and developed synthetically by Yudovich et al. [20] indicate syngenetic origin of La in LCB coals. Low La contents in coals result from coal-forming plants. La in coals comes probably from mineral matter aggregates of terrigenous origin from weathering zones of granitoid rocks and pegmatites in the north-eastern alimentation area.

Scandium

Sc contents in LCB coals is significantly higher than Sc content in the coals of the LSCB and international coals (Tab. 2). A wide change interval in Sc content in the coals and high standard deviation indicate extensive variability in Sc occurrence in the coals both in the profile and within the LCB. The highest Sc contents of the profile of the Lublin Formation were found in the coals from the seams 394 and 378, while the lowest values in the coals from the seam 391 (Fig. 2). In the profile of the seams (Tab. 1), higher Sc contents, as compared with other parts, were noted in the centre (seams 394 and 378) and in the floor and the roof of the seams (391 and 382). Large differences in Sc contents in the coals within the LCB were found in the seams 394>391=387.

Correlation coefficients indicate that there is a considerable influence by organic matter on average Sc content in the investigated LCB coals (Tab. 3). In organic matter probably Sc co-occurs with Be>Ni>Cr>V>Cu>Y>CoSb>Pb, while it occurs quite rarely with Zn>W>Mo. Presence of Sc in the coals excludes the occurrence of phosphorus. Following Yudovich et al. [20], it was assumed that Sc derives from coal-forming plants which absorbed it from solubilized aggregates of pegmatite grains and mafic minerals.

Table 2 Average values (ppm) of La, Sc, U and Th in coals from research areas

Element	Range	Arithmetic mean	Geometric mean	Standard deviation	Mean of World	Other bituminous coals in Poland
La	33 - 213	79.24	70.40	45.42	1–40 ⁷ ; 3–10 ¹⁰ ;	
Th	9 - 54	28.76	26.80	10.75	4 ⁷ ; 3.5±0.7 ¹⁰ ;	USCB: 2.3 ⁵ ;
U	10 - 45	15.76	14.21	8.70	2.0 ⁷ ; 1.9±0.1 ¹⁰ ;	LSCB: 1500-9900 ³ ; 1202-1360 ⁴ ; USCB: 8.9-6720 ² ; 37-7200 ³ ; 0.3 ⁵ ; 0.6-2660 ⁶ ; 0.3 ⁸ ; 0.79-1.52 ⁹ ;
Sc	6 - 133	58.58	49.19	32.65	4 ⁷ ; 3±0.2 ¹⁰ ;	LSCB: 2.41 ¹ ;

Citation of results from: 1 – Golschmidt and Peters [3], 2 – Hoffmann [4], 3 – Jęczalik [5], 4 – Nielubowicz and Wróblewski [10], 5 – Rózkowska [12], 6 – Sałdan [15], 7 – Swaine [17], 8 – Widawska-Kuśmierska [18], 9 – Winnicki [19], 10 – Yudovich et al. [20]. LCB - Lublin Coal Basin, LSCB – Lower Silesian Coal Basin, USCB – Upper Silesian Coal Basin.

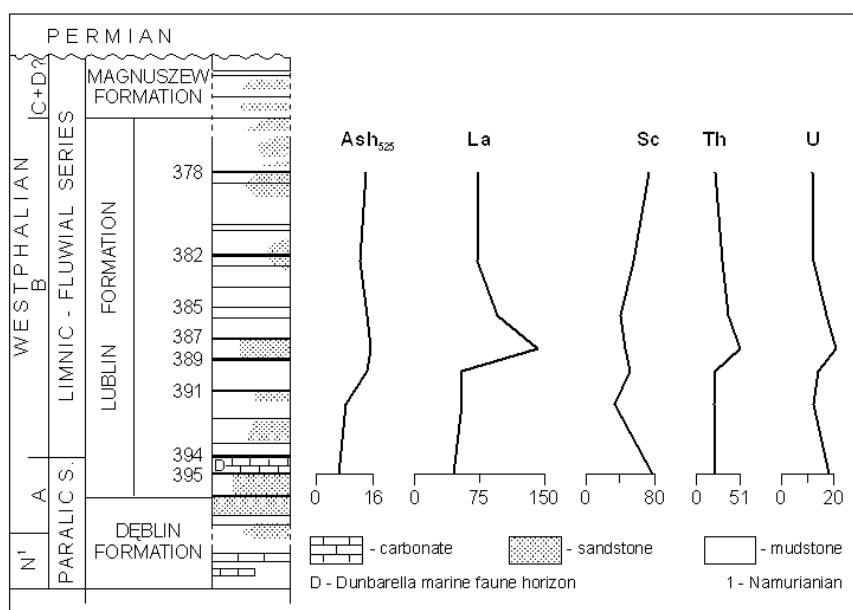


Fig. 2 La, Sc, U and Th content in coal seams in vertical profile of the Lublin Formation (LCB).

Thorium

Average Th content in the LCB coals is significantly lower as compared with USCB coals and international coals (Tab. 2). Th distribution in the coals of the profile of the Lublin Formation is generally 1-modal, with maximum Th content in the coals of the seam 387, and minimum in the coals of the seam 391 (Fig. 2). Coals in the parts near the roof of the coal seams are slightly enriched in Th.

Correlation coefficients indicate that probably mineral matter gains importance over organic matter in Th concentration (Tab. 3). Following Yudovich et al. [20], Th was assumed to concentrate more in minerals from weathering igneous and metamorphic rocks from alimentionation areas of the LCB than in coal organic matter. Undoubtedly, in mineral aggregates Th often co-occurs with La>Ba>Nb>Sr>Ti>Al=Zr, while quite rarely with Sn and P. Presence of Th in the coals excludes the occurrence of Mg>Mn>FeNa>As.

Uranium

Average U content in the LCB coals is higher than its content in international bituminous coals, however, it is generally lower than U content in the LSCB and USCB coals (Tab. 2). In general, U content in the coal seams of the profile of the Lublin Formation is weakly differentiated, with maximum U content is the coals of the seam 387 (Fig. 2). In the profile of the coal seams small differences of uranium content were noted as well (Tab. 1).

Correlation coefficients indicate the relationship between U and organic portion of the investigated coals. Following Yudovich and Ketris [21], it was assumed that U in coals probably occurs in organic complex compounds and solutions of humic and fulvonic acids, in association with clay mineral aggregates.

Table 3 Values of correlation coefficient between the contents of La, Yh, U, Y and Sc in coals and coals ash content from the LCB and correlations relationships between the elements. Correlation coefficient for confidence interval 95% is $r = \pm 0.35$

Element	La	Sc	Th	U
Ash₅₂₅	0.01	-0.49	0.25	-0.26
Ag	0.23	-0.17	-0.01	-0.32
Al	0.22	0.01	0.53	0.01
As	-0.17	0.00	-0.35	-0.02
Ba	0.38	-0.23	0.65	-0.18
Be	0.13	0.79	-0.03	0.51
Bi	-0.18	0.07	-0.31	-0.07
Ca	-0.12	0.04	-0.21	-0.10
Cd	-0.04	-0.10	0.01	-0.08
Co	0.23	0.63	-0.06	0.23
Cr	0.37	0.75	0.13	0.08

Cu	0.45	0.72	0.20	0.55
Fe	-0.27	0.12	-0.47	0.05
K	-0.13	-0.15	-0.11	-0.07
La	1.00	0.20	0.75	0.18
Mg	-0.48	0.13	-0.66	0.02
Mn	-0.39	0.06	-0.65	0.01
Mo	-0.01	0.37	-0.25	0.42
Na	-0.21	-0.23	-0.36	-0.07
Nb	0.58	0.27	0.63	0.40
Ni	0.17	0.77	-0.15	0.26
P	0.15	-0.35	0.40	-0.16
Pb	0.34	0.59	0.20	0.36
Sb	0.06	0.61	-0.15	0.59
Sc	0.20	1.00	0.02	0.33
Sn	0.40	-0.09	0.45	0.12
Sr	0.27	-0.33	0.59	-0.20
Th	0.75	0.02	1.00	0.12
Ti	0.29	0.04	0.58	-0.02
U	0.18	0.33	0.12	1.00
V	0.50	0.72	0.30	0.54
W	0.28	0.37	0.21	0.10
Y	0.42	0.67	0.34	0.37
Zn	-0.11	0.44	-0.26	0.39
Zr	0.50	-0.02	0.52	0.25

Conclusions

Contents of La, Sc, Th and U in LCB coals are markedly higher as compared with international coals, and higher (Sc and Th) and lower (U) as compared with other Polish Carboniferous coal basins. Lanthanum in Polish coals was determined for the first time. Distribution of ash, La and Th contents in the coals of the Lublin Formation is 1-modal, and contents of Sc and U are 2-3 modal. There is variation in the contents of ash, and La, Sc, Th and U in the coals in the profile of some coal seams, which are caused by sorption and different element diffusion rates. Organic matter has a fundamental influence on the contents of Sc and U in the coals; Th content is affected by mineral matter and La by both organic and mineral matter to the same extent. The elements derived probably from

granitoid rocks and pegmatitoids from NE Poland. In the LCB coals, La, Sc, Th and U occur in associations with elements marked by geochemical relationships.

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